

The University of Chicago

I. A KINETIC STUDY OF THE
CHROMIC ACID OXIDATION OF
ISOPROPYL ALCOHOL

II. THE IODINATION OF FIBROIN

A PART OF A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE PHYSICAL
SCIENCES IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
JUNE, 1943

By
AARON NOVICK

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This work was made possible by the guidance of Professor F. H. Westheimer. The author is indebted to him for a stimulating, yet exact, introduction to scientific research.



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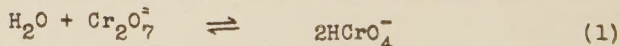
PART I

A KINETIC STUDY OF THE CHROMIC ACID OXIDATION OF ISOPROPYL ALCOHOL

INTRODUCTION

This thesis describes a kinetic investigation of the oxidation of isopropyl alcohol to acetone by chromic acid in acid solution. The kinetic method has been a powerful tool in enabling chemists to obtain a more complete understanding of the mechanism of many chemical reactions. For example, a great deal is known, largely from such evidence, about the mechanism of solvolytic reactions. Oxidations, however, are usually kinetically more complex; and consequently, little is really known about them. Besides this possible theoretical interest, much useful practical information may be gained from a rate study. One of the reasons for selecting chromic acid as the oxidizing agent, therefore, is that it is a commonly used reagent. The oxidation of isopropyl alcohol was chosen since the reaction goes to completion, has a convenient half-life, and the oxidation product, acetone, is stable toward further oxidation by chromic acid.

There have been a number of kinetic studies made of oxidations, but all of them have been incomplete in several respects. Apparently, the equilibrium which exists among the chromium-containing ions in an aqueous solution of chromic acid has been quite generally overlooked. Also, few have paid attention to the role of hydrogen ion in the reaction. And finally, most of the studies were not made at constant ionic strength. These factors have been considered in the present study. The equilibrium



which exists in aqueous solutions of chromic acid has been taken into account. Moreover, the effect of hydrogen ion concentration on the rate, as well as the influence of the concentration of chromate and of alcohol, was studied. Possible interference from salt effects was eliminated by conducting the investigation at a constant ionic strength.

A preliminary investigation by Professor F. H. Westheimer,¹

¹F. H. Westheimer, Unpublished work.

employing a calorimetric technique, indicated that the reaction is fourth order, the approximate rate expression being

$$-\frac{d[\text{CrO}_3]}{dt} = k_4[\text{CrO}_3][\text{CH}_3\text{CHOHCH}_3][\text{H}^+]^2 \quad (2)$$

where k_4 is the fourth order rate constant.

The present study was made at an ionic strength of 0.400 and at 40° C. Measurement of the rate was made by withdrawing aliquot samples of a reaction mixture from time to time and titrating the unreduced chromate iodometrically.

The kinetic data obtained indicated that the reaction is fourth order. However, analysis of the results in the light of the knowledge of the equilibrium (1) showed that the oxidizing agent is the acid chromate ion (HCrO_4^-). The rate expression should then be written as follows:

$$-\frac{d[\text{HCrO}_4^-]}{dt} = k_4[\text{HCrO}_4^-][\text{CH}_3\text{CHOHCH}_3][\text{H}^+]^2 \quad (3)$$

Evidence was also obtained for the occurrence during the reaction of a chromium valence state, intermediate between that in chromic salts and that in chromates. A tentative mechanism, based on the observed kinetics and the intermediate valence state, is proposed in this paper.

HISTORICAL

The earliest significant kinetic study of a chromic acid oxidation was that of Jabłozyński¹ who studied the rate of oxidation of oxalic acid by chromic acid. He reported that the reaction was first order with respect to chromic acid. His first order "constants," however, increased with time. Many other examples of chromate oxidation have been reported in the literature. In practically every case, the reactions were reported to be first order with respect to chromate. The reactions included oxidation

¹C. Jabłozyński, Z. anorg. Chem., **60**, 38 (1908).

of arsenious acid,¹ oxalic acid,² nitrous acid,³ aniline,⁴ isopropyl alcohol,⁵ acetaldehyde,⁶ lactic acid,⁷ iodide ion,⁸ anthracene,⁹ succinic acid,¹⁰ formic acid,¹¹ ferrous ion,¹² alkaloids,¹³ and aromatic aldehydes.¹⁴ Solvents used included water, acetic acid, and aqueous sulfuric acid. Vavon and Zaremba,¹⁵ who studied the oxidation of isopropyl alcohol, reported rising values of their first order rate "constants"; and they ascribed this increase to simultaneous oxidation of acetone. This explanation is not accepted here since no reduction of chromic acid by acetone under the conditions employed in our study could be observed. An alternative explanation will be apparent later.

No agreement was found by various investigators in regard to the substance being oxidized. In several cases there are different kinetic orders reported for the same substance. For oxalic acid, Dhar¹⁶ reported the order to be three with respect to the

¹R. E. DeLury, J. Physic. Chem. **11**, 47 (1907).

²N. R. Dhar, J. Chem. Soc., **111**, 707 (1907).

³A Kurtenacker, Chem. Abs., **16**, 3421 (1922).

⁴J. Piccard and F. Montmollin, Helv. chim. acta., **6**, 1021 (1923).

⁵B. V. Tronov, V. F. Udodov, and M. I Chizhova, Zentralblatt **281**, 2924 (1928); G. Vavon and C. Zaremba, Bull. soc. chim., **49**, 1853 (1931).

⁶G. Lejeune, J. Chim. phys., **24**, 391 (1927).

⁷C. Wagner, Z. anorg. allgem. Chem., **168**, 279 (1928).

⁸R. F. Beard and N. W. Taylor, J. Amer. Chem. Soc., **51**, 1973 (1929).

⁹V. Majer and V. Marecek, Z. physik. Chem. **A159**, 181 (1932).

¹⁰H. C. S. Snethlage, Rec. trav. chim., **60**, 199 (1941).

¹¹Hans Ammann-Brass, Chem. Abs., **32**, 423 (1938).

¹²R. Lang, Mikrochim. Acta, **3**, 113 (1938).

¹³L. J. Heidt, J. Amer. Chem. Soc., **61**, 3455 (1939).

¹⁴G. Lucchi, Chem. Abs., **36**, 6880 (1942).

¹⁵Vavon and Zaremba, op. cit.

¹⁶Dhar, op. cit.

organic acid, while Snethlage¹ found a value of two. Oxidations have been reported which are first order with respect to arsenious acid,² nitrous acid,³ aniline,⁴ acetaldehyde,⁵ iodide ion,⁶ a series of aliphatic alcohols,⁷ succinic acid,⁸ formic acid,⁹ and a number of aromatic aldehydes.¹⁰ Beard and Taylor¹¹ observed both first and second order reactions for iodide ion. Dey and Dhar¹² found the oxidation of tartaric, maleic, and succinic acids to be second order with respect to these acids. Heidt¹³ gave one-half for the order with respect to a number of alkaloids containing secondary alcohol groups.

There has been little study made of the dependence of rate on hydrogen ion concentration. DeLury,¹⁴ from his investigation of the oxidation of arsenious acid, obtained 1.4 for the kinetic order with respect to hydrogen ion. His study was made, however, in sulfuric acid solution where the concentration of hydrogen ions is not readily or accurately calculated. Kurtenacker¹⁵ described two reactions as occurring in the oxidation of nitrous acid, one second order and one independent of hydrogen ion. In a

¹Snethlage, op. cit.

²DeLury, op. cit.

³Kurtenacker, op. cit.

⁴Piccard and Montmollin, op. cit.

⁵Lejeune, op. cit.

⁶Beard and Taylor, op. cit.

⁷Tronov, Udodov, and Chichova, op. cit.

⁸Snethlage, op. cit.

⁹Ammann-Brass, op. cit.

¹⁰Lucchi, op. cit.

¹¹Beard and Taylor, op. cit.

¹²A. N. Dey and N. R. Dhar, Z. Elektrochem., 32, 586 (1926).

¹³Heidt, op. cit.

¹⁴DeLury, op. cit.

¹⁵Kurtenacker, op. cit.

more recent study, Beard and Taylor¹ found that the oxidation of iodide ion by chromate proceeds by two mechanisms, one second order with respect to hydrogen ion, and the other, first order.

In regard to the mechanism of the reaction, there has been some discussion of intermediate chromium valence states. Jabłozyński² postulated a stepwise reduction of chromate through the valence states five and four. The first real experimental basis for such intermediates was obtained by Wagner.³ He treated potassium dichromate in acid solution with ferrous ion and then added the solution to a solution of potassium iodide in sodium bicarbonate. Free iodine was liberated. Wagner interpreted this experiment as an indication of the presence of an intermediate valence state of chromium. Furthermore, he stated that the intermediate, because it could oxidize iodide ion in alkaline solution, was a stronger oxidizing agent than hexavalent chromium. He further observed this intermediate to be quite unstable; since if he added his dichromate, ferrous ion solution to a solution of sodium bicarbonate and then added potassium iodide after about one minute, little or no free iodine was obtained. In order to find the valence state of this intermediate, Wagner titrated the iodine formed in the first experiment. He found that two atoms of iodine were liberated for each ferrous ion oxidized. From this he concluded that the oxidation of ferrous ion to ferric ion leads to a pentavalent chromium compound which can then oxidize two iodide ions to iodine. Wagner obtained similar liberation of iodine by adding solutions of dichromate and lactic or oxalic acids to bicarbonate and iodide. Again he explained the phenomenon as due to an intermediate of valence state five, but he did not confirm this hypothesis by titration of the liberated iodine. Chromium of valence state four was postulated by Ammann-Brass⁴ as an intermediate in the photochemical dichromate oxidation of formic acid. Further evidence was given by Lang⁵ who observed that although chromic acid will

¹Beard and Taylor, op. cit.

²Jabłozyński, op. cit.

³Wagner, op. cit.

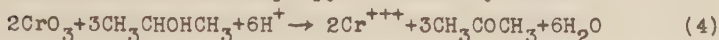
⁴Ammann-Brass, op. cit.

⁵Lang, op. cit.

not oxidize ferroine (ferrous ortho phenanthroline complex), addition of arsenious acid to chromic acid gives a solution which will oxidize ferroine to ferriine, giving the well known color change. He concluded that the intermediate was one involving tetra-valent chromium. Finally, additional support for intermediate chromium valence states was furnished by Stefanovskii and Zanko¹ who observed a hump in the electrometric titration curve of chromic acid by a number of reducing agents. This, they ascribed to the existence of more powerful intermediate oxidizing agents.

RESULTS

The oxidation of isopropyl alcohol by chromic acid



was observed to go to completion. Practically quantitative analyses were obtained for acetone by precipitation as the 2,4 dinitrophenylhydrazone; and furthermore, no oxidation of acetone by chromic acid was observed under the conditions employed in this rate determination.

Experiments were also carried out to find any unusual effects that might interfere with the complete investigation. Apparently visible light has no effect on the reaction since experiments made in the dark and in the light gave identical rates. This is illustrated in Figure 1. (These runs were made with alcohol and hydrogen ion concentrations very large with respect to chromic acid, so that the reaction is essentially first order with respect to chromic acid.) In addition, a number of cations were investigated for catalytic activity. The ions studied were those reported in the literature to have effects on other chromic acid oxidations. No influence on the rate was found for Cr^{+++} , Fe^{+++} , and Al^{+++} . Mn^{++} , however, reduced the rate about fifty per cent. A dark brown precipitate which was identified as manganese dioxide formed during the course of the run but redissolved when the reaction was allowed to go to completion. The significance of this precipitate will be discussed later. The cation effects are sum-

¹V. F. Stefanovskii and A. M. Zanko, Acta Physicochim. U.R.S.S. 9, 395 (1938).

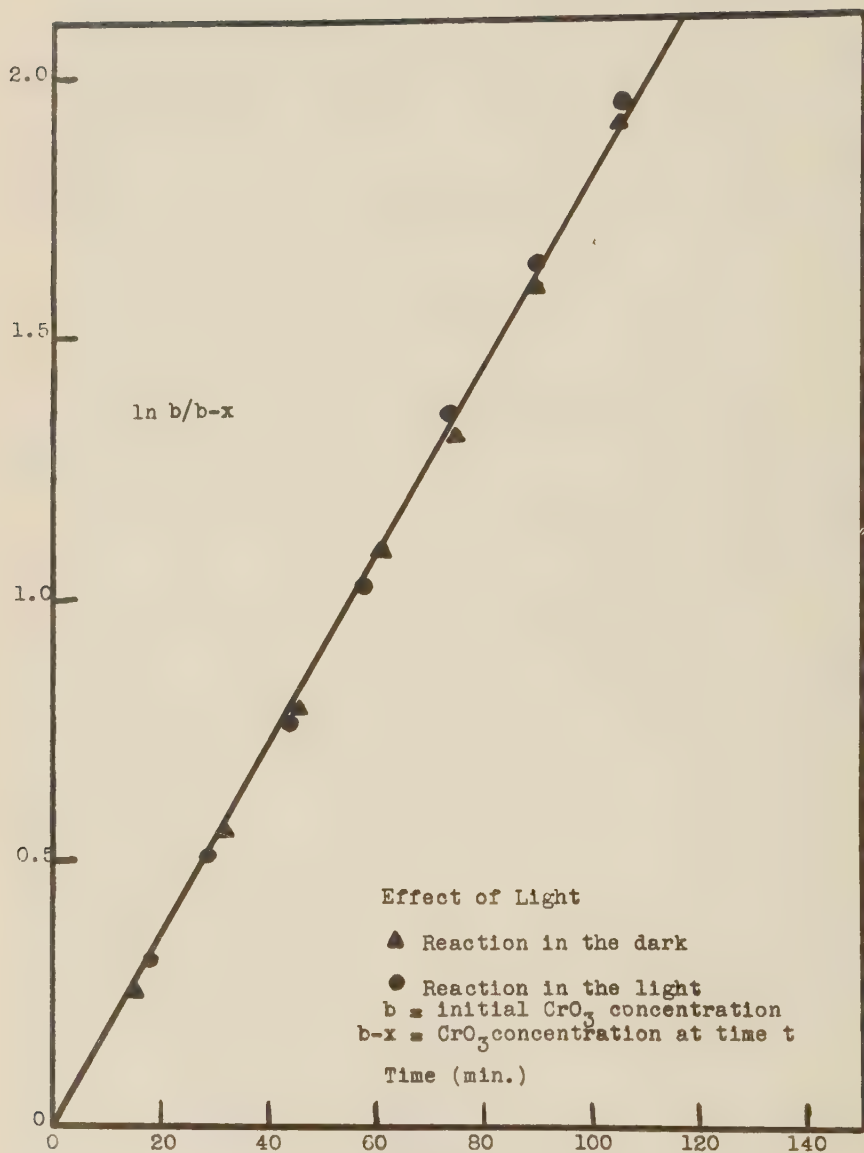


Figure 1

marized in Figure 2.

A strong acid was obviously needed as a source of hydrogen ions. Hydrochloric, perchloric,¹ and benzenesulfonic acids seemed suitable at first. But when equivalent runs were made with these three acids, it was found that perchloric and benzenesulfonic acids give the same rate while hydrochloric acid reduces the rate about thirty per cent. This was ascribed to a specific chloride ion effect, and hence chloride ion was avoided in the rate study. Figure 3 shows graphically the results obtained for each acid.

Determination of Kinetic Order

Chromic acid.--In order to determine the order with respect to chromic acid, a series of experiments was made using the same initial concentrations of alcohol and hydrogen ion in each. In every case the alcohol and hydrogen ion concentrations were more than twenty times the concentration of chromic acid, so it is seen that the concentration of alcohol and hydrogen ion remained practically constant throughout each determination. Hence, if such experiments are carried out over a range of chromic acid concentrations, the variation in rate will be due solely to the variation in chromic acid concentration.

Under these conditions, the equation

$$-\frac{d(\text{CrO}_3)}{dt} = k_4(\text{CrO}_3)(\text{CH}_3\text{CHOHCH}_3)(\text{H}^+)^2 \quad (2)$$

reduces essentially to

$$-\frac{d(\text{CrO}_3)}{dt} = k_1(\text{CrO}_3) \quad (5)$$

where

$$k_1 = k_4(\text{CH}_3\text{CHOHCH}_3)(\text{H}^+)^2 \quad (5')$$

The values of k_4 were actually obtained, however, by integrating equation (2); almost identical values would have resulted from the use of (5) and (5').

¹One might think that the perchloric acid would interfere with the iodometric titration, but no oxidation of iodide ion by 0.400 N perchloric acid was observed. Perchloric acid is an oxidizing agent only in concentrated solution.

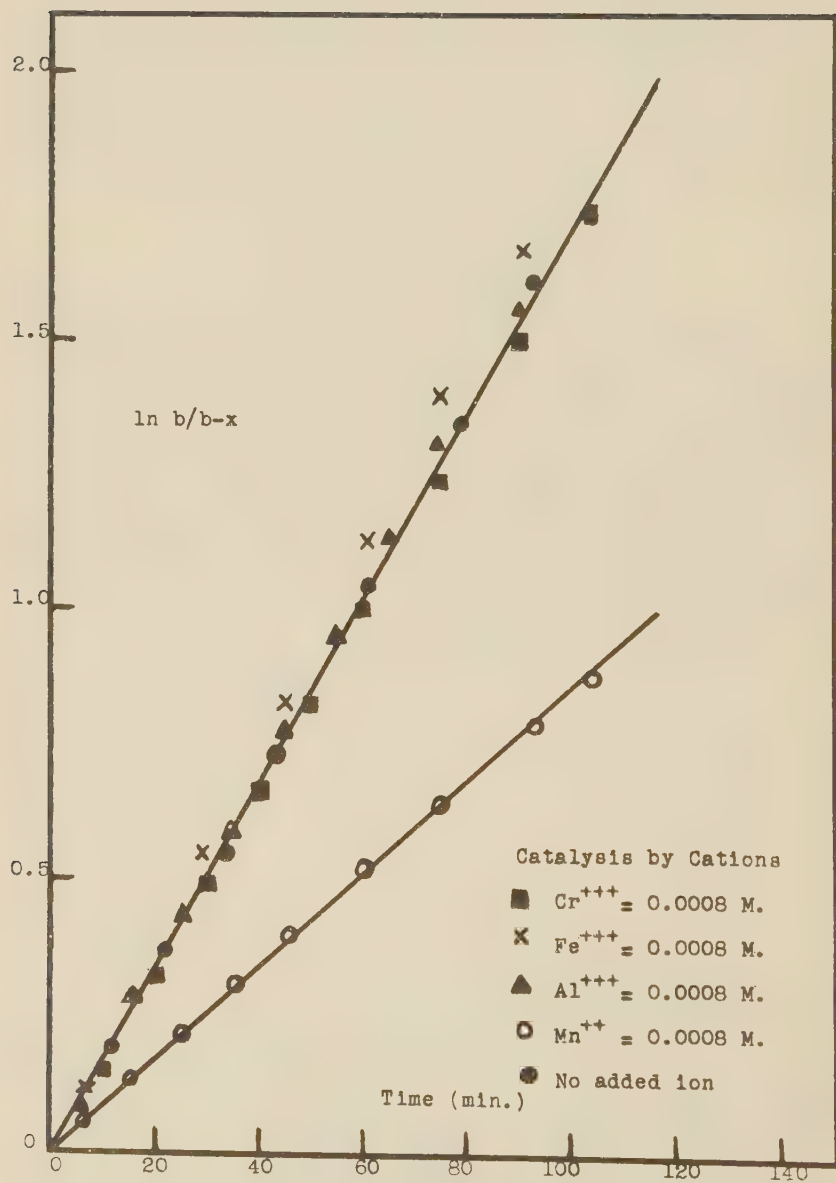


Figure 2

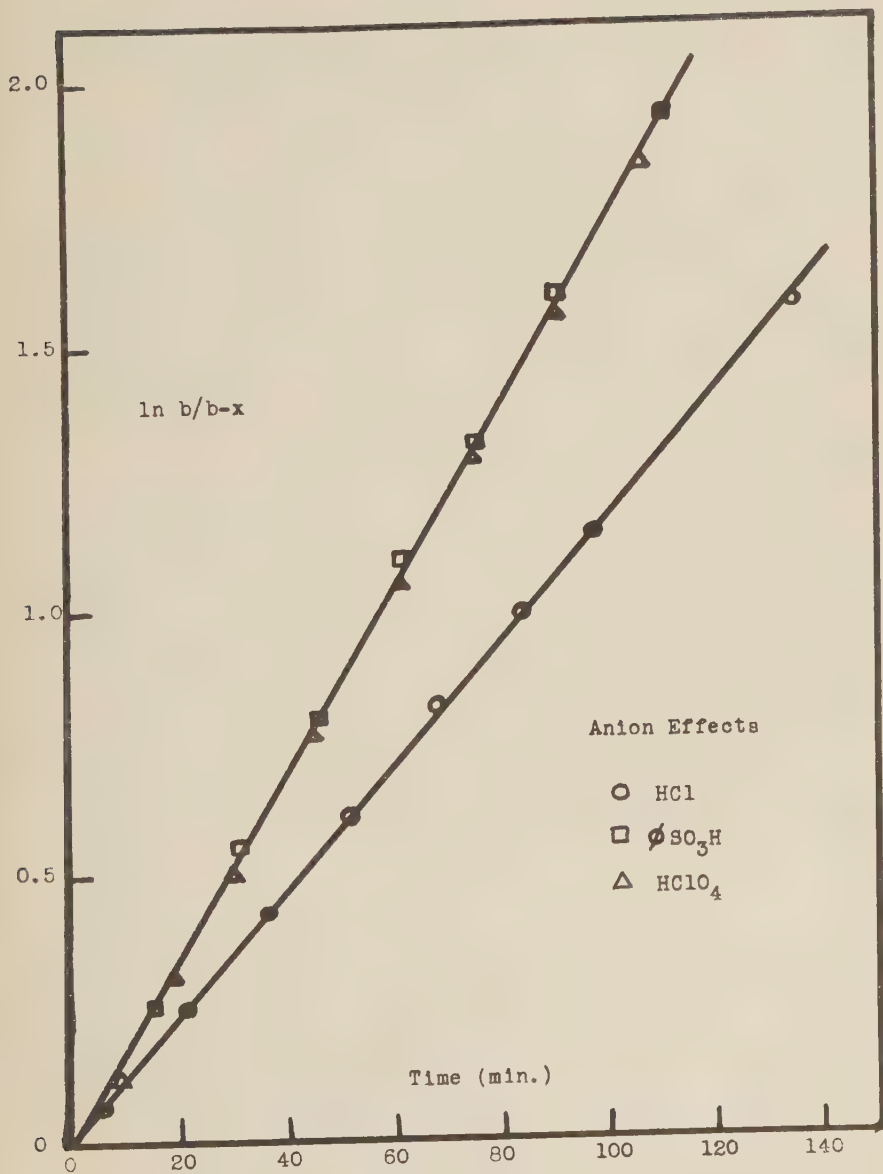


Figure 3

Upon integration, equation (2) becomes

$$-k_4 t = \int_{(\text{CrO}_3)_0}^{(\text{CrO}_3)_t} \frac{d(\text{CrO}_3)}{(\text{CrO}_3)(\text{CH}_3\text{CHOHCH}_3)(\text{H}^+)^2} \quad (6)$$

where $(\text{CrO}_3)_0$ is the initial concentration of CrO_3 , and $(\text{CrO}_3)_t$ is the concentration at time t .

The determination of the value of the integral on the right hand side of this equation is given in the mathematical appendix. It is important to note that when the value of this integral is plotted against time, a straight line of slope k_4 will be obtained if the reaction is first order with respect to chromic acid. The choice of the exponents for alcohol and hydrogen ion will not interfere with this plot since their concentrations remain practically constant during the course of an experiment.

The results obtained for determinations involving chromic acid concentrations from 0.04316 M to 0.0005316 M are given in graphical form in Figure 4. It is seen that satisfactory agreement with equation (4) is obtained over the range from 0.0005316 M to 0.004316 M. But it is also seen that with the more concentrated solutions of chromic acid the rate constant is less and that lines of increasing curvature are obtained.

This disparity in these latter experiments can be explained by considering what ions exist in a solution of chromic acid. Sherrill¹ reported the equilibrium



to exist in aqueous solutions of CrO_3 . This equilibrium is independent of the hydrogen ion concentration. It is not necessary to include the ion $\text{HCr}_2\text{O}_7^{-}$ since Klotz², using a spectrophotometric method,³ found the second ionization constant of dichromic acid

¹M. S. Sherrill, J. Amer. Chem. Soc., **29**, 1641 (1907).

²I. M. Klotz, Unpublished work.

³Ibid., Ph. D. dissertation, University of Chicago, 1940.

to be large.

Now it is obvious that in more concentrated solutions the relative concentration of $\text{Cr}_2\text{O}_7^{=}$ is greater, and the relative concentration of HCrO_4^- is less. Since experimentally the rate constant is greater in the dilute solution where HCrO_4^- predominates, it is logical to assume that HCrO_4^- is the important oxidizing agent, and that $\text{Cr}_2\text{O}_7^{=}$ contributes little (or perhaps nothing) to the reaction rate.

Further qualitative evidence for the hypothesis that acid chromate ion is the principal oxidizing agent is found in the curvature in the graphs representing the reactions employing more concentrated solutions of chromic acid. Neuss and Rieman¹ have reported a value of 0.023 for the equilibrium constant, K, for equation (1)

$$K = \frac{(\text{HCrO}_4^-)^2}{(\text{Cr}_2\text{O}_7^{=})} \quad (6)$$

A calculation using this constant showed that in an experiment starting with 0.04316 M chromic acid, the concentration of acid chromate ion changes during the first half-life from thirty-four to forty-five per cent of the total chromic acid. However, for a determination involving an initial chromic acid concentration of 0.0005316 M, acid chromate ion changes only from ninety-four to ninety-six per cent of the total hexavalent chromium. On the basis of the hypothesis that acid chromate ion is the principal oxidizing agent, it would be expected that the experiment using 0.00053 M chromic acid would show a large rate constant, and that the graph of the integral of equation (5) against time would be a straight line. On the other hand, the experiment using 0.043 M chromic acid would show a much lower rate constant, but the graphs of the integral of equation (5) against time should be concave upward. This is exactly what is found experimentally. Moreover, this hypothesis would also explain in a like fashion the rising values of the rate constants reported by earlier workers and described in the historical section.

This qualitative picture can be supplemented by a more

¹J. D. Neuss and W. Rieman, J. Amer. Chem. Soc., **56**, 2238 (1934).

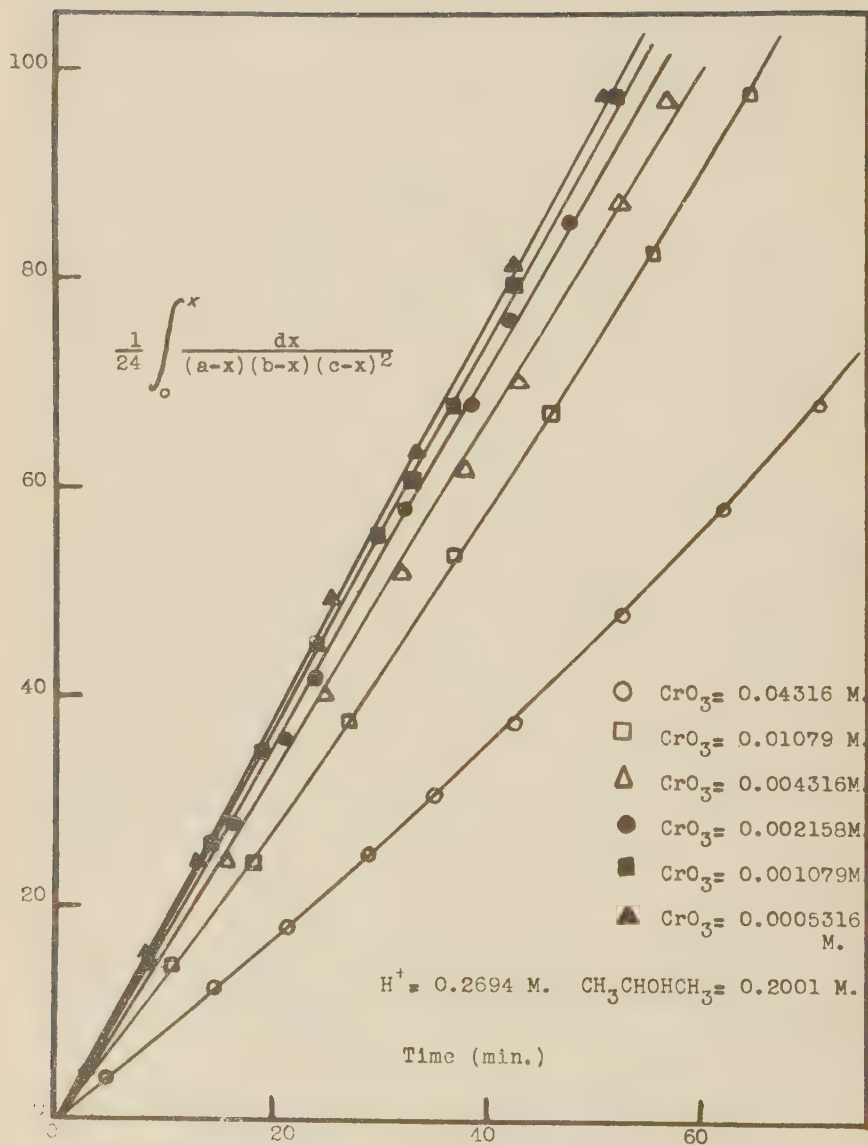


Figure 4

quantitative argument. If it is assumed that acid chromate ion is the oxidizing agent, then the true rate expression becomes

$$-\frac{d(\text{HCrO}_4^-)}{dt} = K_4(\text{HCrO}_4^-)(\text{CH}_3\text{CHOHCH}_3)(\text{H}^+)^2 \quad (3)$$

In order to integrate this equation, the concentration of acid chromate ion must be determined. It is possible to compute this concentration by the use of the equilibrium constant for reaction (1). Several workers have assigned values of the thermodynamic constant, K . Sherrill¹ reported it to be 0.013, Saal² gave 0.019, Neuss and Riemann³ obtained 0.023, and Robinson⁴ found 0.050. All of these determinations were made at 25° C. For this problem, the value of Neuss and Riemann was selected. However, any value of the concentration constant, K' , chosen for 40° C. and an ionic strength of 0.400, must necessarily be an approximation. The computation of the concentration of the acid chromate ion, given in the mathematical appendix, was based on a constant of 0.015. The reasons for the selection of this value are presented in the appendix.

The resultant rate expression, stated in terms of acid chromate ion concentration, was integrated graphically, since analytical methods proved too complex. When the results of the integration (cf. equation 23) were presented graphically, straight lines of almost identical slope were obtained over the whole concentration range. These lines are illustrated in Figure 5, and the corresponding values of the fourth order rate constant are given in Table 1. From this satisfactory agreement over an eighty fold range of chromic acid concentrations, it was concluded that the oxidation is first order with respect to acid chromate ion.

¹Sherrill, op. cit.

²R. N. J. Saal, Rec. trav. chim., 47, 73, 264 (1928).

³Neuss and Riemann, op. cit.

⁴R. A. Robinson, J. M. Wilson, and R. H. Stokes, Trans. Farad. Soc., 37, 566 (1941).

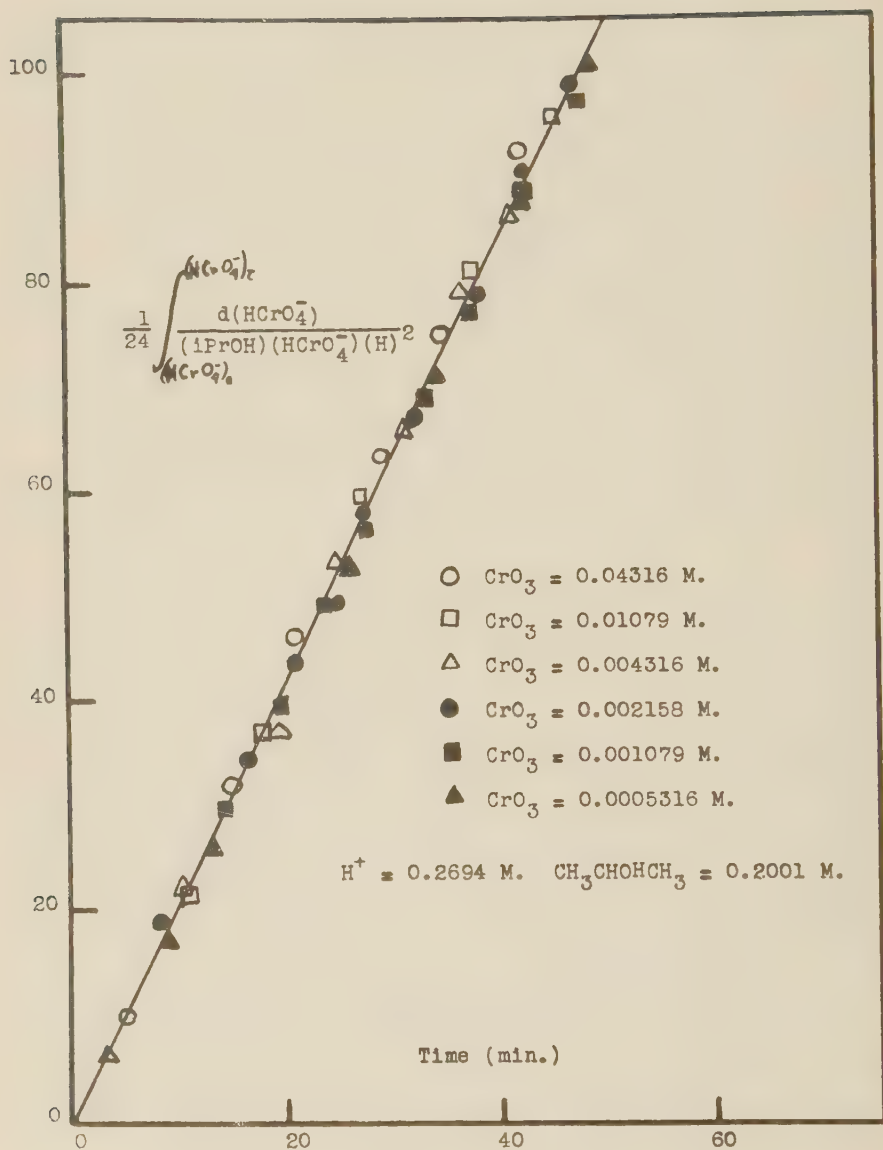


Figure 5

TABLE 1

$$[H^+] = 0.2694 \quad [CH_3CHOHCH_3] = 0.2001$$

$$K' = 0.015$$

$[CrO_3]$ init.	k_4 (moles per liter) ⁻³ min. ⁻¹
0.04316 molar	2.25
0.01079 molar	2.10
0.004316 molar	2.05
0.002158 molar	2.03
0.001079 molar	2.06
0.0005316 molar	2.02

Isopropyl alcohol.--In order to determine the kinetic order with respect to isopropyl alcohol, a series of experiments were made at the same initial concentration of chromic acid and hydrogen ion, while the concentration of alcohol was varies from determination to determination. As in the preceding case, the concentrations of hydrogen ion and alcohol were kept large with respect to chromic acid so that the reaction was almost first order with respect to acid chromate ion. And again, since in each run the initial concentration of hydrogen ion and chromic acid was not varied, any variation in rate was due solely to isopropyl alcohol. The observed variation in rate can be satisfactorily explained by an expression first order with respect to alcohol. This is shown in Table 2 which gives values of the fourth order rate constant found over a twenty-fold range of alcohol concentration. The slight increase in rate constant with increase in alcohol concentration may be due to the change in the dielectric constant of the medium.¹

TABLE 2

$[H^+] = 0.2694$	$[CrO_3] = 0.002158$
$[CH_3CHOHCH_3]$	k_4 (moles per liter) ⁻³ min. ⁻¹
0.02001	1.90
0.04002	1.90
0.08004	1.96
0.2001	2.03
0.4002	2.21

¹George Scatchard and L. F. Epstein, Chem. Rev., **30**, 211 (1942).

Hydrogen ion.---A similar approach was used to find the order with respect to hydrogen ion. This time initial alcohol and chromic acid concentrations were kept constant in each experiment, while the initial concentration of hydrogen ion was varied over a twelve fold range. Again the reaction was studied as one which is approximately first order in acid chromate ion, since in each case the concentration of alcohol and hydrogen ion were kept large in comparison with chromate. The variation in rate found, which must be due only to hydrogen ion, corresponds to a rate expression 1.87 order in hydrogen ion. Apparently the principal reaction is second order in hydrogen ion; hence, values of the fourth order rate constants were calculated on this basis and are given in Table 3.

TABLE 3

$$[\text{CrO}_3] = 0.001079$$

$$[\text{H}^+]$$

0.4000
0.2694
0.1200
0.05280
0.03200

$$[\text{CH}_3\text{CHOHCH}_3] = 0.2001$$

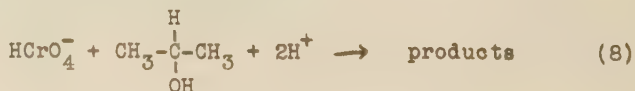
$$k_4 (\text{moles per liter})^{-3} \text{ min.}^{-1}$$

2.04
2.06
2.30
2.90
3.60

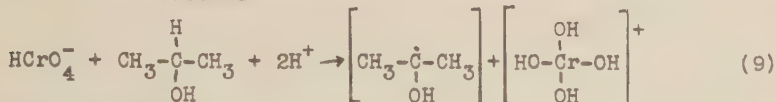
The deviation from exactly integral order could be explained by a simultaneous reaction, first order with respect to hydrogen ion. For the determinations involving the higher concentrations of hydrogen ion, it is seen that the reaction is almost exactly second order. It is only with the more dilute acid that significant departure from second order occurs, and this is what should be expected since a first order reaction would become relatively more important with decreasing hydrogen ion concentration.

DISCUSSION

The kinetics found in this investigation indicate that the rate-determining step involves one molecule of isopropyl alcohol, one acid chromate ion, and two hydrogen ions. This reaction can be represented by the equation

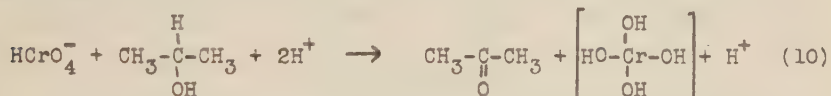


There are two possible types of products. The reaction might involve a one electron transfer and go by a free-radical type mechanism. The products would be then a ketyl free radical and an intermediate containing chromium of valence five. The equation then becomes



The products, written in brackets because they are not isolated and are only hypothetical, would react in some rapid fashion to give the final products, acetone and chromic ion.

Alternatively, the reaction might involve a two electron change in the rate-determining step and lead to an ionic mechanism. The products would then be acetone and a chromium compound of valence four.



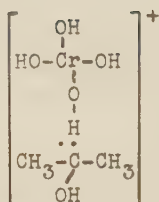
Again, it would be assumed that the hypothetical intermediate reacts in some fast manner to yield chromic ions.

Besides the kinetic support for these types of interpretation, further substantiation is given by evidence found for the existence of some intermediate valence state of chromium.

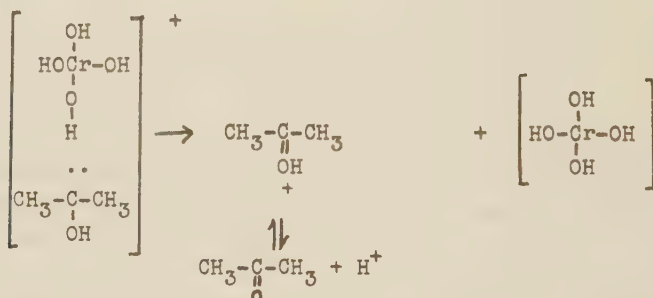
In the description of the results of the catalytic experiments, it was mentioned that a precipitate of manganese dioxide is formed when the reaction is carried out in the presence of manganous ion. Chromic acid itself in acid solution or in solution with acetone, chromic ions, and hydrogen ion, will not oxidize manganous ion to manganese dioxide. Therefore, it must be concluded that some intermediate is formed in the oxidation of isopropyl alcohol which can oxidize manganous ion. This type of evidence has been given for other reactions involving the reduction of chromate, as has been seen in the historical section.

No conclusive choice of mechanism can be made from the evidence obtained to date since the valence state of the intermediate chromium compound is undetermined. However, a simple reasonable picture can be given for the ionic mechanism. One is faced with the task of constructing the formula for an activated complex containing one acid chromate ion, one molecule of isopropyl alcohol, and two hydrogen ions. This could be done by writing the

structure below.



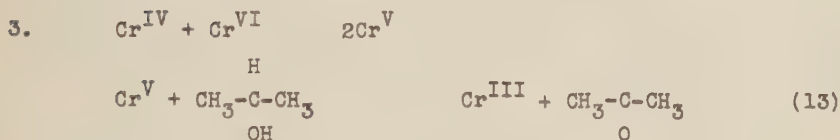
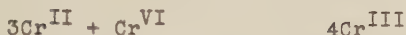
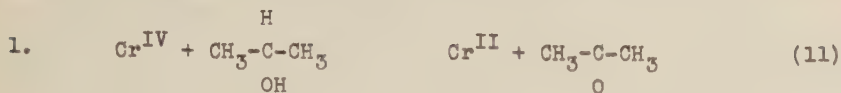
This is a likely picture since it involves a symmetrical distribution of the hydrogen ions. Moreover, a sensible reaction of decomposition can be written for this intermediate. This reaction would involve removal of the hydrogen opposite the hydroxyl group and two electrons by the chromium group, giving as products the oxonium ion of acetone (which is of course in equilibrium with free acetone and hydrogen ion), and an intermediate chromium compound of valence four. Below is a schematic picture of the reaction.



The mechanism is consistent in that it involves placing the center of positive charge on the group which must remove the negative fragment, a hydrogen with two electrons. Moreover, it is in agreement with the experimentally observed fact that HCrO_4^- rather than $\text{Cr}_2\text{O}_7^{2-}$ is the oxidizing agent. This mechanism would favor acid chromate ion since addition of two hydrogen ions to HCrO_4^- gives a positive ion and to $\text{Cr}_2\text{O}_7^{2-}$ gives a neutral molecule. It would be expected that a positive ion would more readily remove the negative "hydride ion" than would a neutral molecule.

No attempt is made to describe the nature of the hypothetical chromium compound. It may exist as some negative ion in equilibrium with the structure given. This tetra-valent state, it is postulated, would react in some rapid fashion to give chromic

ions. There are a variety of possible reactions; some of them are given below:



EXPERIMENTAL

Preparation of materials.--Chromic acid was prepared by recrystallization of c.p. chromic acid from water. The method used was essentially that given by Archibald.¹ The recrystallized sample, which gave negative tests for sulfate and halide, was dried for several weeks in vacuo over calcium chloride.

Anhydrous isopropyl alcohol was prepared by refluxing the constant boiling mixture over fresh lime for four hours. The alcohol was distilled and refluxed again for four hours over a fresh supply of lime. After distillation from the lime, the alcohol was fractionated through an eight plate column. The fraction used came over in the range 82.2-82.3° C. at 751 mm. It had a density of 0.7840 25°/4° and an index of refraction of 1.3758 at 25° C. for the sodium D line. Literature² values for these constants are 82.26° C. (760 mm.) for the boiling point, 0.7830 for the density, and 1.37538 for the index of refraction.

¹E. H. Archibald, "The Preparation of Pure Inorganic Substances," J. Wiley and Sons, Inc., New York, 1932, p. 279.

²A. Weissberger and E. Proshauer, "Organic Solvents," Oxford Press, Oxford, 1935, p. 27.

Baker's analyzed grade perchloric acid was used. Eastman's benzenesulfonic acid was purified in the following fashion. The original acid was neutralized with reagent grade barium hydroxide. The solution was evaporated to obtain the barium salt. This barium salt was twice recrystallized from water. Diluted reagent grade sulfuric acid was carefully added to an aqueous solution of the recrystallized salt until no precipitate of barium sulfate was obtained upon the addition of one drop of dilute acid. The barium sulfate was filtered off and the solution was diluted to approximately one normal.

Sodium perchlorate was obtained by recrystallizing G. F. Smith's sodium perchlorate hydrate twice from water any drying at 150°C . Eastman's sodium benzenesulfonate was purified by recrystallization from water.

Preparation of standard solutions.--All of the acids used were standardized against carbonate-free base. Solutions of chromic acid were made by dissolving weighed samples of well-dried chromic acid and diluting to volume in a volumetric flask. These solutions were checked iodometrically against standard thiosulfate solution, and they agreed to within 0.2 per cent with the calculated normality. Standard solutions of isopropyl alcohol were prepared by dissolving in water carefully weighed samples of the anhydrous alcohol and diluting to a standard volume. Neutral salt solutions were made by dissolving weighed quantities of the well-dried salt.

Technique used in making the rate study.--The kinetic runs were conducted in a well insulated water thermostat. A mercury regulator was used, and the heating element was controlled by a vacuum tube operated relay. Temperature was held constant at 39.92°C . (checked against a Bureau of Standards thermometer) to within 0.002° for a single experiment and was not allowed to vary by more than 0.005° during the entire study.

A flask and jacketed pipet of the type described by Westheimer and Metcalf¹ were used in the rate study.

Desired quantities of chromic acid, perchloric acid, and sodium perchlorate solutions were pipetted into a 250 ml. volumetric flask. This flask and the bottle containing the standard al-

¹F. H. Westheimer and R. P. Metcalf, J. Amer. Chem. Soc., **63**, 1339 (1941).

cohol solution were then placed in the thermostat for one hour to bring them to temperature. Then the desired quantity of alcohol was pipetted into the volumetric flask, and the flask was quickly diluted to volume with water at thermostat temperature. The time at which the alcohol was added to the volumetric flask was called zero time. The contents were quickly transferred to a 250 ml. Erlenmeyer flask, which was clamped in position in the thermostat. A self-leveling pipet, of about 10 ml. capacity, which had been calibrated before use, was filled by means of a compressor bulb. This pipet was surrounded by a jacket through which water from the thermostat was circulated. After rinsing the pipet several times with the reaction solution, a sample was withdrawn into a sodium iodide solution at time, t . The liberated iodine was titrated with standard thiosulfate according to the usual method.¹ The concentration of chromic acid was computed for time t from this titration.

Completeness of reaction.--Fifty milliliters of 1.190 N HClO_4 , 25 ml. of 2.001 M isopropyl alcohol, and 25 ml. of 0.1079 M CrO_3 were added to a 250 ml. volumetric flask; and the mixture was diluted to volume. This reaction solution was allowed to stand at 40°C . for 48 hours. A fifty milliliter sample was withdrawn and analyzed for acetone by the method of Iddles and Jackson.² This method involves precipitation of the 2,4 dinitrophenylhydrazone from a cold saturated solution of 2,4 dinitrophenylhydrazine in 2 N. HCl . In one experiment, 0.1887 gm. of hydrazone (m.p. 124.5°C . - 125°C . lit. m.p., 126°C .³) was obtained. This corresponded to 97.9 per cent recovery since the yield calculated from the initial concentration of chromic acid was 0.1927 gm. When samples of analytically pure acetone were analyzed by this method, analyses ranging from 96 to 98 per cent were obtained.

Effect of light.--An experiment was made using 0.01079 M chromic acid, 0.2001 M isopropyl alcohol, and 0.2694 M hydrogen ion. The reaction was conducted first in the dark, and then a

¹W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," J. Wiley and Sons, Inc., New York, 1940, p. 199.

²H. A. Iddles and C. E. Jackson, Ind. Eng. Chem. Anal. Ed., 6, 454 (1934).

³N. R. Campbell, Analyst, 61, 393 (1936).

second experiment was made under the illumination of a 250 watt lamp placed 30 centimeters away.

Catalytic effects.--Experiments, using 0.01079 M chromic acid, 0.2001 M isopropyl alcohol, and 0.2694 M hydrogen ion, were made in the presence of 0.0008 M Cr^{+++} , Fe^{+++} , Al^{+++} , and Mn^{++} ions.

Identification of manganese dioxide.--A solution was made containing 20 ml. of 1.079 M CrO_3 , 15 ml. of 2.001 M isopropyl alcohol, 25 ml. of 0.20 M MnCl_2 , and 40 ml. of 1.190 N HClO_4 . This solution was held at 40°C . for one hour and then filtered. The precipitate was washed well with water and then with dry acetone. It was then dried at 110°C . for 24 hours. Qualitative analysis showed manganese to be the only cation present. Manganese dioxide was suspected. This was confirmed by two independent methods of analysis.

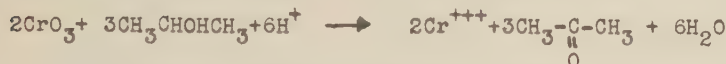
First a weighed sample of dried precipitate was treated with excess standard sodium oxalate in acid solution, and the excess oxalate titrated with permanganate according to Mellor.¹ A sample of the precipitate weighing 0.0898 gm. analyzed for 0.0739 gm. of MnO_2 . This corresponds to 72.4% MnO_2 ; if it is assumed that the difference is due to water of hydration, the formula would be $\text{MnO}_2 \cdot 1.03 \text{H}_2\text{O}$. This is reasonable since it is known that manganese dioxide forms this indeterminate type of hydrate. Confirmation was obtained by an independent analysis for manganese. This was done by analyzing a weighed sample of precipitate by oxidation to permanganate ion with sodium bismuthate according to the method given in Hillebrand and Lundell.² A sample of the precipitate weighing 0.0774 gm. showed 0.0399 gm. of manganese on analysis. Since this would correspond to 81.8 per cent MnO_2 in the precipitate, in agreement with the first analysis, all of the manganese in the precipitate was in the form of the dioxide.

¹J. W. Mellor and H. V. Thompson, "Quantitative Inorganic Analyses," C. Griffin and Co., London, 1938, p. 404.

²W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," J. Wiley and Sons, Inc., New York, 1929, p. 346.

MATHEMATICAL APPENDIX

The stoichiometric equation for the oxidation of isopropyl alcohol by chromic acid in acid solution is



Assuming a fourth order equation leads to the rate expression

$$-\frac{d(\text{CrO}_3)}{dt} = k_4 [\text{CrO}_3][\text{CH}_3\text{CHOHCH}_3][\text{H}^+]^2 \quad (2)$$

which upon substitution, becomes

$$-\frac{d(\text{CrO}_3)}{dt} = \frac{d(\text{Cr}^{+++})}{dt} = \frac{dx}{dt} = k_4 (b'-x)(a'-\frac{3}{2}x)(c'-4x)^2 \quad (14)$$

where a' = initial concentration of isopropyl alcohol in moles per liter

b' = initial concentration of chromic acid in moles per liter

c' = initial concentration of hydrogen ion in moles per liter

x = concentration of chromic ion at time, t

A simple algebraic transformation lead to

$$\frac{dx}{dt} = 24 k_4 (b-x)(a-x)(c-x)^2 \quad (15)$$

where

$$a = \frac{2}{3} a'$$

$$b = b'$$

$$c = \frac{c'}{4}$$

Integration of this equation from $t = 0$ to $t = t$ and

$x = 0$ to $x = x$ gives the expression

$$\int_0^x \frac{dx}{(a-x)(b-x)(c-x)^2} = 24 k_4 t \quad (16)$$

This integration can be performed by partial fractions. The result is

$$J \ln \frac{a}{a-x} + K \ln \frac{b}{b-x} + M \ln \frac{c}{c-x} + \frac{Lx}{c(c-x)} = 24k_4 t \quad (17)$$

$$\text{where } J = \frac{1}{(b-a)(c-a)^2}$$

$$K = \frac{1}{(a-b)(c-b)^2}$$

$$L = \frac{1}{(c-a)(c-b)}$$

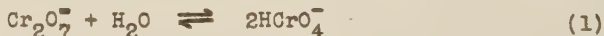
$$M = \frac{2c-b-a}{(c-a)^2(c-b)^2}$$

This equation (17) was used for the curves shown in Figure 4. The value of the expression on the left was plotted against t .

It has been shown in this paper that the proper rate expression must depend on the concentration of acid chromate ion rather than the total chromic acid concentration. Hence, the proper rate expression is

$$-\frac{d[\text{HCrO}_4^-]}{dt} = k_4 [\text{HCrO}_4^-] [\text{CH}_3\text{CHOHCH}_3] [\text{H}^+]^2 \quad (4)$$

The value of the concentration of acid chromate ion at time, t , may be obtained from the equilibrium



The thermodynamic equilibrium constant, K , may be expressed in terms of the concentration constant, K' , and the activity coefficient of each ion, γ ion.

$$K = \frac{(\text{HCrO}_4^-)^2}{(\text{Cr}_2\text{O}_7^{2-})} = \frac{[\text{HCrO}_4^-]^2 \gamma_{\text{HCrO}_4^-}}{[\text{Cr}_2\text{O}_7^{2-}] \gamma_{\text{Cr}_2\text{O}_7^{2-}}} = K' \frac{\gamma_{\text{HCrO}_4^-}}{\gamma_{\text{Cr}_2\text{O}_7^{2-}}} \quad (7)$$

This gives for the value of K'

$$K' = K \frac{\gamma_{\text{Cr}_2\text{O}_7^{2-}}}{\gamma_{\text{HCrO}_4^-}^2}$$

The activity coefficients for HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions were approximated by literature values of the coefficients for Cl^{-1} and SO_4^{2-} ions, respectively. Thus, K' becomes

¹R. A. Robinson, J. Amer. Chem. Soc., **63**, 1011 (1941).

²H. S. Harned and M. A. Cook, J. Amer. Chem. Soc., **61**, 495 (1939).

$$K' = 0.023 \frac{0.290}{(0.691)^2} = 0.014$$

Although this figure is not very accurate, it does not matter too much since the final results are not very sensitive to the value of this constant. In the actual computations, K' was chosen as 0.015.

One can then solve for the concentration of acid chromate ion by means of the equation

$$K' = \frac{[\text{HCrO}_4^-]^2}{[\text{Cr}_2\text{O}_7]} = \frac{[\text{HCrO}_4^-]^2}{1/2 \{(b-x) - [\text{HCrO}_4^-]\}} \quad (19)$$

where $b-x$ is the total chromic acid concentration at time t . This leads to the quadratic equation

$$[\text{HCrO}_4^-]^2 = 1/2 K' \{ (b-x) - [\text{HCrO}_4^-] \} \quad (20)$$

the solution for which is

$$[\text{HCrO}_4^-] = \frac{-1/2 K' + \sqrt{1/4 K'^2 + 2K' (b-x)}}{2} = \frac{-K' + \sqrt{K'^2 + 8K' (b-x)}}{4} \quad (21)$$

The differential rate expression then becomes

$$\frac{dx}{dt} = 24k_4 (a-x)(c-x)^2 \left[\frac{-K' + \sqrt{K'^2 + 8K' (b-x)}}{4} \right] \quad (22)$$

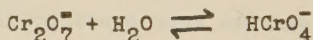
and the integrated equation

$$6k_4 t = \int_0^x \frac{dx}{(a-x)(c-x)^2 \left[\frac{-K' + \sqrt{K'^2 + 8K' (b-x)}}{4} \right]} \quad (23)$$

The indicated integration was performed graphically. The results were used to obtain the curves in Figure 5, and the values of k_4 in Table 1.

SUMMARY

A kinetic investigation of the oxidation of isopropyl alcohol to acetone by chromic acid at 40° C. is described. The data obtained indicated that the reaction is fourth order: first order with respect to alcohol, first order with respect to chromic acid, and second order with respect to hydrogen ion. More careful analysis of the results, however, in the light of the knowledge of the equilibrium



obtaining in aqueous solutions of chromic acid, showed that the principal oxidizing agent is acid chromate ion (HCrO_4^-). Hence, the rate expression is given by

$$-\frac{d[\text{HCrO}_4^-]}{dt} = k_4[\text{HCrO}_4^-][\text{CH}_3\text{CHOHCH}_3][\text{H}^+]^2$$

Evidence was also obtained for the occurrence during the reaction of a chromium compound of valence state intermediate between that in chromic salts and that in chromates. A tentative mechanism, based on the observed kinetics and the intermediate chromium valence state, is proposed.

